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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US93/08833 <b>(22) International Filing Date:</b> 17 September 1993 (17.09.93) <b>(30) Priority data:</b> 07/954,539 29 September 1992 (29.09.92) US <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US). <b>(72) Inventors:</b> BRANT, Patrick ; 103 Harborcrest, Seabrook, TX 77586 (US). CANICH, Jo, Ann, Marie ; 900 Henderson Avenue, Apt. 808, Houston, TX 77058 (US). DIAS, Anthony, Jay ; 1411 Quite Green Court, Houston, TX 77062 (US). BAMBERGER, Robert, Lee ; 15903 Sea Palms, Crosby, TX 77532 (US). LICCIARDI, Gary, Frederick ; 20003 Big Timber, Humble, TX 77346 (US). HENRICHS, Paul, Mark ; 2209 Maconda, Houston, TX 77027 (US).	<b>(74) Agents:</b> BUTTS, Evan, K. et al.; Exxon Chemical Company, P.O. Box 5200, Baytown, TX 77522 (US). <b>(81) Designated States:</b> AU, CA, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG CHAIN BRANCHED POLYMERS		
<b>(57) Abstract</b> <p>A novel polymer and process for producing polymers incorporating linear long chain side branches are provided. The long chain linear branches occur at a frequency of less than 5.0 branches per 1000 carbon atom of the main polymer chains with at least some branches having a molecular weight greater than the critical molecular weight for entanglement of the polymer. The linear long chain branched polymers are produced by alpha-olefin macromolecule incorporation during bridged metallocene catalyst polymerization in solution and slurry processes. The polymers are characterized by superior processability characteristics of the polymer melts and superior mechanical characteristics of the solid polymers. The polymers are useful for fabrication into a wide variety of articles by conventional fabrication techniques.</p>		

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TITLE

5 LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG  
CHAIN BRANCHED POLYMERS

FIELD OF THE INVENTION

10 This invention relates to the field of long chain  
branched polymers and a process to make them.

BACKGROUND OF THE INVENTION

15 This invention relates to novel polyolefin  
polymers, processes for producing such polymers, and  
applications for such polymers. The commercial  
significance of polyolefin polymers is enhanced by the  
variety of forms they may take which often exhibit  
different physical properties. These different  
20 properties make polyolefin polymers useful in many  
different end use applications. The structural  
features of polyolefins that are considered most  
significant are molecular weight, which is related to  
polymer chain length, the type and tacticity of side-  
chain branches, and the distribution of side-chain  
25 branches along the main polymer chains. Over the  
years, considerable attention has been given to the  
molecular architecture of polyolefins. Polyolefins can  
be commercially produced using any one of a number of  
processes. The random nature of most polymerization  
30 processes results in a heterogeneous polymer, rather  
than a truly homogeneous polymer product. Polyolefins  
produced by classical Ziegler-Natta catalysts consist  
of mixtures of molecules of different molecular weights  
and different amounts of comonomer incorporation.  
35 These differences result from the differences in  
catalysts used, and differing rates of comonomer  
incorporations. Other factors influencing polymer

products include choice of monomers, catalyst reactivity or ability to incorporate comonomers, and differing polymerization process conditions.

Commercial polyethylenes fall into one of two  
5 general categories, linear polyethylenes (LPES) and  
"conventional" low density polyethylenes (LDPEs). LPES  
are traditionally produced by addition polymerization  
of ethylene, or by the copolymerization of ethylene and  
an alpha-olefin comonomer, in a variety of processes  
10 using coordination catalysts. LDPEs are traditionally  
produced by free-radical polymerization of ethylene in  
high temperature and high pressure reactors using  
peroxide initiators. These two broad categories of  
polyethylenes have significant structural and physical  
15 differences. The most important difference between  
LPES and LDPEs is the nature of the side-chain  
branching. LDPEs are highly side-chain branched having  
dendritic (tree-like) long chain side branches attached  
to the main polymer chains. These branches are created  
20 as a result of inter-molecular chain transfer during  
free-radical polymerization. Dendritic side-chain  
branching gives certain advantages, particularly  
processing advantages, to the polymer melts. However  
these processing advantages are balanced by  
25 disadvantages inherent with LDPEs relating to  
mechanical properties of the solid polymers such as  
lower stiffness, hardness, low tear resistance, low  
environmental stress crack resistance (ESCR) and, low  
tensile strength. These properties relative to LPES  
30 with equivalent density and melt index properties.

Likewise, LPES without long chain side branches  
have good mechanical properties such as good stiffness,  
hardness, tensile strength characteristics, tear  
resistance, and ESCR; however, from a processing  
35 standpoint, LPES have the disadvantages of a tendency  
to melt fracture and low shear sensitivity resulting in

high melt viscosity, low melt strength and higher processing costs.

Polyethylene producers have spent considerable time and resources over the years trying to produce  
5 polymers possessing the polymer melt processing advantages of LDPEs and the mechanical properties advantages of solid LPEs. Most efforts have centered around adding long branches to LPEs. One conventional  
10 method of producing long chain branches in LPEs is to copolymerize ethylene with alpha-omega dienes. This method is illustrated in U.S. Patent 3,984,610, PCT application 91-17,194 and Japanese KOKAI 02-261,809, which are incorporated by reference herein.

In this method, dienes are simultaneously  
15 incorporated into propagating chains, thereby creating a covalent bridge between two linear molecules. The resulting structure in the vicinity of the bridge is typically shaped like the letter "H". The resultant side-chain branches can be long and are usually paired  
20 rather than isolated. As the number of dienes per molecule increases, the complexity of the branching approaches that of dendritic branching ultimately causing the polymer to lose its linear mechanical characteristics. In addition to mechanical properties  
25 shortcomings, polymers produced with dienes have encountered resistance to approval by regulatory authorities for food contact applications.

Other methods to produce long chain branches on LPEs involve post-polymerization treatments of linear  
30 molecules. Several different types of post-polymerization treatments have been used. United Kingdom Patent 901,148 demonstrates the production of branched polyethylene by treating molten polyethylene with oxygen. One method of doing this is by forcing  
35 air into the molten polyethylene during melt extrusion. This method of production results in non-linear long chain branches. United States Patent 4,586,995,

discloses the irradiation of molten polyethylene in the absence of oxygen to produce Y branches having two to fifty carbon chains per ten thousand carbon atoms in the main polymer chain. United Kingdom Patent  
5 1,379,853 discloses the introduction of branches into polyethylene during the degradation of high density polyethylene in the presence of an organic peroxide. This process will result in dendritic side branches. Finally, Japanese Kokai 59-59,760 discusses the  
10 production of long chain branched polyethylene by heating polyethylene containing a terminal vinyl group at 180° - 360°C under vacuum conditions or an inert atmosphere for five minutes to six hours. The polymer produced has long chain branches with a frequency of  
15 3.5 branches per molecule. These branches are non-linear.

A third type of process for producing branching in linear polyethylene is the use of a polymerization cocatalyst which contains a long chain branched  
20 polymeric group. U.S. Patent 4,500,648 and divisionals thereof disclose high density polyethylene production with branches prepared by polymerization of ethylene in the presence of a coordination catalyst containing an organoaluminum compound having a branched polymeric  
25 hydrocarbyl group as one of its substituents. The polymers produced by this method contain non-linear long chain branches.

A method for the preparation of LLDPE using only ethylene is described in European Application Number  
30 87108556.9 EPA 250,999. The method used is the oligomerization of ethylene using nickel based catalysts followed by copolymerization of the olefin mixture with ethylene through use of a chromium catalyst system. The objective of this application is  
35 to utilize a process for preparing higher olefins to prepare a mixture of olefins which is then copolymerized to yield the LLDPE structure. The LLDPE

prepared in this method consists of polyethylene with a distribution of side-chains having 14 to 200 carbon atoms. One deficiency of this application is that it utilizes very low activity catalysts to form the oligomers and the subsequent copolymers. Secondly, this application does not recognize the importance of utilizing even longer side-chains than those described in the application.

A method for producing LLDPE containing long-chain branches is described in European patent application 91301811.5 EPA 446,013 and Japanese application H1-251748. EP 91301811.5 presents the polymerization of ethylene using Nickel complexes to give LLDPE containing long-chain branching. JP H1-251748 presents the copolymerization of ethylene and hexene using Nickel based polymerization catalysts. Using the catalyst systems described in the application, ethylene copolymers containing short and long chain branches are produced. The chief limitations of these applications are those known for Nickel based catalyst systems: 1) the low catalyst activities (30 g polymer/mmol catalyst in 1 hr); and 2) molecular weight distribution is proportional to molecular weight, therefore high molecular weights are accompanied by broad molecular weight distributions. This method does not produce higher Mw with narrow Mw/Mn.

#### SUMMARY OF THE INVENTION

This invention relates to novel polymers and processes for making polymers incorporating linear long chain side branches. The term "linear" is herein defined to include side chains that have some side chain branching but are not dendritic. The linear long chain branches are comprised of sidechains being at least 250 carbons long, which have molecular weights at least as great as the critical molecular weight for entanglement ( $M_c$ ) of the polymer. The linear long



chain branches occur at a frequency of less than 5.0 branches per 1000 carbon atoms in the main polymer chains. The linear long chain branched polymers are produced by incorporating a macromolecule during  
5 metalocene-catalyzed solution polymerization processes (solvent or bulk process at low, medium or high pressure). The long chain branched polymers possess the processability characteristics of conventional long chain branched polymer melts and the mechanical  
10 characteristics of conventional solid linear polymers. Polymers produced in accordance with this invention are useful for fabrication into a wide variety of articles by injection molding, extrusion coating and molding, blown film, cast film, thermoforming and rotational  
15 molding.

#### DETAILED DESCRIPTION OF THE INVENTION

During traditional coordination-catalyst polymerization of polyethylenes, most polymer chains  
20 are terminated by the beta-abstraction mechanism which results in terminal unsaturation. If the molecule terminates after incorporation of a comonomer, the result is vinylene or vinylidene unsaturation. If the molecule terminates after the incorporation of  
25 ethylene, the result is vinyl unsaturation. A vinyl unsaturated molecule can be considered a large alpha-olefin.

Linear copolymers are produced by additional polymerization of two or more vinyl terminated monomers  
30 ranging in size from two to thirty carbon atoms. In the present invention, copolymers are produced in which vinyl terminated polymers, also called macromonomers or macromers, are incorporated into the addition polymerization reaction along with the monomers. The  
35 vinyl terminated polymers responsible for the unique characteristics of polymers produced in accordance with the present invention are molecules having molecular

weights greater than the critical molecular weight for entanglement ( $M_C$ ) of the polymer into which the vinyl terminated polymers are incorporated. The  $M_C$  for polyethylene is 3,800. The vinyl terminated polymers of this invention are 250 or more carbon atoms long, preferably 350 to 3500, even more preferably 300 to 3000, or have a Mw of greater than 6000. Further, the vinyl terminated polymers of this invention are incorporated into the growing polymer at an average frequency of no more than 5 long side chains per 1000 carbon atoms along the main chain, preferably the average frequency is 0.2 to 3 long side chains per 1000 carbon atoms, more preferably 0.9 to 2 long side chains per carbon atoms.

Using traditional coordination catalyst processes, these vinyl terminated polymers do not incorporate into growing polymer chains. The inventors have discovered that using certain metallocene catalysts, preferably under solution process conditions, in accordance with the present invention will result in these vinyl terminated polymers being incorporated into growing polymer chains at controllable amounts of incorporation. As these vinyl terminated polymers are incorporated into propagating polymer chains, they become isolated long chain branches of that polymer chain. The inventors have found that long chain branches, in accordance with the present invention, yield polymers having the positive mechanical attributes of solid linear polyolefins, while having the positive processing characteristics of melts of branched polyolefins.

The vinyl terminated polymers of this invention which eventually become side chains can be homopolymers or copolymers of one or more  $C_2$  to  $C_{30}$  olefin, preferably alpha olefins, even more preferably homo or copolymers of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methylpentene-1. Cyclic

olefins are also useful monomers in the practice of this invention. Likewise, the main chain can also be a homopolymer or copolymer of one or more C<sub>2</sub> to C<sub>30</sub> olefins, preferably alpha olefins, even more preferably homo or copolymers of ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1. Copolymer is herein defined to include polymers of 2 to 4 different monomers and block copolymers of any of the above olefins or alpha olefins.

The vinyl terminated polymers useful in this invention can be prepared using a variety of metallocene catalysts and process conditions. The particular choice of catalyst and process conditions depends upon the desired polymer composition and molecular weights. High vinyl termination content is necessarily preferred. Preferably about 0.9 to about 1.1 chain end unsaturations per macromer are present, even more preferably about 1 chain end unsaturation per macromer. Conditions which favor their formation are high temperatures, no comonomer, no transfer agents like hydrogen, and a non-solution process or a dispersion using an alkane diluent. Thus the metallocene should be active at relatively high temperatures. The selected metallocene may also be thermally activated to yield the beta-hydrogen eliminated product; vinyl ends. Thus one could prepare materials at low temperature then increase the temperature to get the beta-hydride eliminated product. The steric requirements of the metallocene will affect the degree to which copolymerization occurs. Metallocenes which possess steric hindrance will yield vinyl terminated polymers which are relatively free of branches when compared to metallocenes which do not possess this hindrance.

Another method producing vinyl termination involves production of polymer with an ethylene "cap" or end with the needed vinyl group. This could be

accomplished by beginning polymerization at a low temperature, for example, below zero degrees Celsius, and raising the reaction temperature at the "end" of the reaction, for example, to above ten degrees

5 Celsius, and simultaneously adding ethylene so that the ethylene preferentially polymerizes to form an end "cap" or block. A block copolymer of ethylene and a C<sub>3</sub> to C<sub>30</sub> alpha olefin would also present the necessary vinyl termination.

10 The vinyl terminated polymers can be optimally copolymerized using metallocenes which are sterically unhindered. In addition the polymerization system should be a single-phase, or if two-phase, the vinyl terminated polymers must be sufficiently mobile to  
15 permit their copolymerization. The preferred process for their copolymerization is a solution process. Thus the process solvent and temperature preferred are those in which the vinyl terminated polymer is soluble or substantially swollen.

20 The present invention preferably utilizes catalyst system comprising a metallocene catalyst with cocatalyst activators of an alumoxane or a "non-coordinating" anion. The metallocene catalyst is an activated cyclopentadienyl group 4 transition metal  
25 compound. In particular, the metallocene catalysts employed in this invention are organometallic coordination compounds which are cyclopentadienyl derivatives of group 4 metals of the periodic table of the elements and include mono-, di- and tri-  
30 cyclopentadienyls and their derivatives. Particularly desirable are the metallocenes of the group 4 metals: titanium, zirconium and hafnium. The cyclopentadienyl metallocenes of this invention can be activated with either an alumoxane or a "non-coordinating" anion-type  
35 activator. In general at least one metallocene compound is employed in formation of the catalyst system. Metallocenes employed in accordance with this

invention contain at least one cyclopentadienyl ring and preferably comprise titanium, zirconium, or hafnium, most preferably hafnium, or zirconium for bis-cyclopentadienyl compounds and titanium for mono-cyclopentadienyl compounds. The cyclopentadienyl ring can be substituted or unsubstituted or contain one or more substituents e.g. from 1 to 5 substituents such as for example, hydrocarbyl substituent e.g. up to five C<sub>1</sub> to C<sub>20</sub> hydrocarbyl substituents or other substituents e.g. for example, a trialkyl cyclic substituent. A metallocene may contain 1, 2 or 3 cyclopentadienyl rings, however, two rings are preferred for use with hafnium or zirconium. One ring is preferred for use with titanium.

The catalyst system used in this invention can be described as comprising cyclopentadienyl transition metal catalyst having at least one delocalized pi-bonded moiety and an activating cocatalyst. The catalyst system used in this invention can also be described as comprising a cyclopentadienyl transition metal catalyst of a transition metal compound containing a single cyclopentadienyl group and a heteroatom containing group each bonded to the transition metal, said cyclopentadienyl group and heteroatom containing groups optionally bridged through a divalent moiety and an activating cocatalyst.

In another embodiment of the present invention the macromonomer can be polymerized in a gas phase process. This may be achieved by pre-polymerizing the macromonomer by one of many methods known in the art. For example, the method for supporting a catalyst known in U.S. Patent Application 885,170 filed 5-18-92, incorporated by reference, discloses how to place a catalyst on a support. This supported catalyst can then be combined with the macromonomer under appropriate polymerization conditions to pre-polymerize the macromonomer with the supported catalyst. This

combination can then be introduced into a gas phase polymerization reactor to produce long chain branched polymers in this invention.

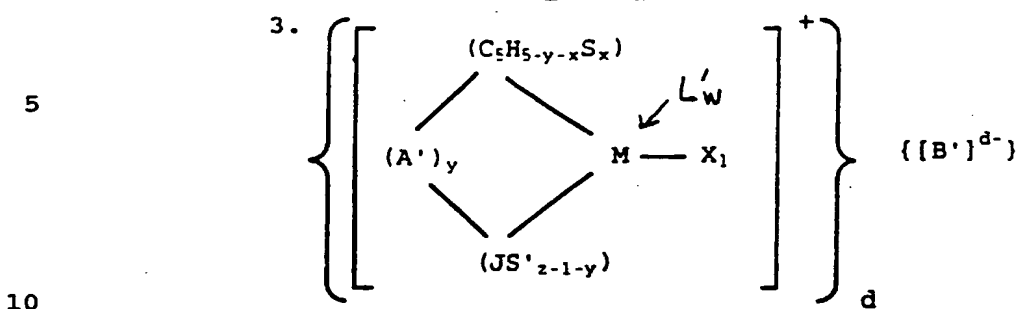
This macromonomer may also be pre-polymerized with  
5 other traditional gas phase supported catalysts and  
similarly introduced into the gas phase polymerization  
reactor. Likewise, one could use a two step process  
wherein the macromonomer or the catalyst is first  
placed on support using techniques known in the art and  
10 then the catalyst and/or the macromonomer are added later  
to form the supported pre-polymerized catalyst  
combination. As is well known in the art, the pre-  
polymerization process is normally a slow, controlled  
process to initiate controlled polymer fracture or  
15 support fracture thus, one of ordinary skill in the art  
would be sure to maintain appropriate reaction  
conditions such as temperatures from 40°C to 140°C in a  
suitable solvent with the introduction of ethylene, or  
suitable comonomers to form the macromonomers in a  
20 controlled amount.

#### Ionic Catalyst System - General Description

The process of this invention is practiced with  
that class of ionic catalysts referred to, disclosed,  
25 and described in European Patent Applications EP 0 277  
003 A1 and EP 0 277 004 A1, and PCT Application WO  
92/00333, and U.S. Patents 5,055,438 and 5,096,867,  
which are herein incorporated by reference. The ionic  
catalysts used in this invention can be represented by  
30 one of the following general formulae (all references  
to groups being the new group notation of the Periodic  
Table of the Elements as described by Chemical and  
Engineering News, 63(5), 27, 1985):

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1.  $[[[(A-Cp)MX_1]^+]_d] ([B']^{d-})$
2.  $[[[(A-Cp)MX_1L]^+]_d] ([B']^{d-})$



wherein:

(A-Cp) is either (Cp) (Cp\*) or Cp-A'-Cp\*; Cp and Cp\* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 element, substituted Group 16 element or halogen radicals, or Cp and Cp\* are cyclopentadienyl rings in which any two adjacent S groups are joined forming a C4 to C20 ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp\* rings or (C<sub>5</sub>H<sub>5-y-x</sub>S<sub>x</sub>) and JS'(<sub>z-1-y</sub>) groups;

(C<sub>5</sub>H<sub>5-y-x</sub>S<sub>x</sub>) is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

M is titanium, zirconium, or hafnium;

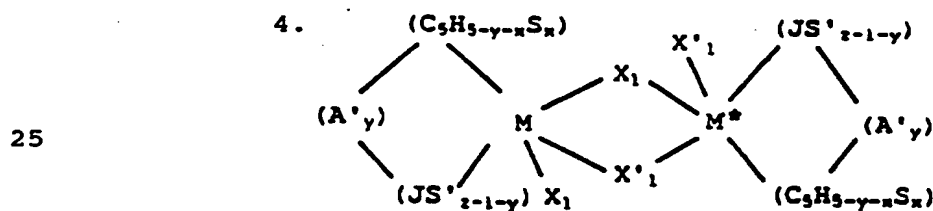
X<sub>1</sub> is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-

substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L or all or any M, S, or S';

(JS<sub>z-1-y</sub>) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

y is 0 or 1;

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal center M and M\* are bridged by X<sub>1</sub> and X'<sub>1</sub>, wherein M\* has the same meaning as M and X'<sub>1</sub> has the same meaning as X<sub>1</sub> where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by the formula:



w is an integer from 0 to 3;

B is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms or an anionic Lewis-acid activator resulting from the reaction of a Lewis-acid activator with the precursor to the cationic portion of the catalyst system described in formulae 1-4. When B' is a Lewis-acid activator, X<sub>1</sub> can also be an alkyl group donated by the Lewis-acid activator; and

d is an integer representing the charge of B.



The improved catalysts are preferably prepared by combining at least two components. In one preferred method, the first component is a cyclopentadienyl derivative of a Group 4 metal compound containing at least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group 4 metal compound (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or metalloid atom or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallocarboranes.

In general, suitable anions for the second component may be any stable and bulky anionic complex having the following molecular attributes: 1) the anion should have a molecular diameter greater than 4 Å; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within the core of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing to oxidizing agent. Anions meeting these criteria - such as polynuclear boranes, carboranes, metallocarboranes, polyoxoanions and anionic coordination complexes are well described in the chemical literature.

The cation portion of the second component may comprise Bronsted acids such as protons or protonated Lewis bases or may comprise reducible Lewis acids such as ferricinium, tropylium, triphenylcarbenium or silver cations.

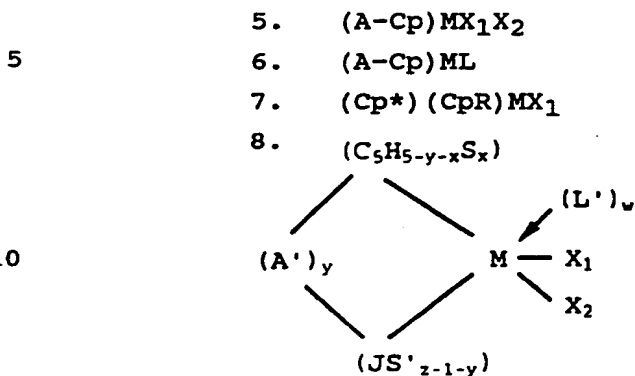
In another preferred method, the second component is a Lewis-acid complex which will react with at least one ligand of the first component, thereby forming an ionic species described in formulae 1-4 with the ligand abstracted from the first component now bound to the second component. Alumoxanes and especially methylalumoxane, the product formed from the reaction of trimethylaluminum in an aliphatic or aromatic hydrocarbon with stoichiometric quantities of water, are particularly preferred Lewis-acid second components.

Upon combination of the first and second components, the second component reacts with one of the ligands of the first component, thereby generating an ion pair consisting of a Group 4 metal cation and the aforementioned anion, which anion is compatible with and "non-coordinating" toward the Group 4 metal cation formed from the first component. The anion of the second compound must be capable of stabilizing the Group 4 metal cation's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization. The catalysts of this invention may be supported. U.S. Patents 4,808,561, issued 2-28-89; 4,897,455 issued 1-3-90; 5,057,475 issued 10-15-91; and U.S. Patent Application 459,921 (published as PCT International publication WO 91/09882) disclose such supported catalysts and the methods to produce such and are herein incorporated by reference.

#### A. The Metallocene Component

The Group 4 metal compounds; i.e., titanium, zirconium, and hafnium metallocene compounds, useful as first compounds in the preparation of the improved catalyst of this invention are cyclopentadienyl derivatives of titanium, zirconium and hafnium. In

general, useful titanocenes, zirconocenes, and hafnocenes may be represented by the following general formulae:



wherein:

15 (A-Cp) is either (Cp)(Cp\*) or Cp-A'-Cp\*; Cp and Cp\* are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-

20 hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 elements, substituted Group 16 elements or halogen radicals, or Cp and Cp\* are

25 cyclopentadienyl rings in which any two adjacent S groups are joined forming a C<sub>4</sub> to C<sub>20</sub> ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

R is a substituent on one of the cyclopentadienyl radicals which is also bonded to the metal atom;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp\* rings or  $(C_5H_{5-y-x}S_x)$  and  $JS'(z-1-y)$  groups;

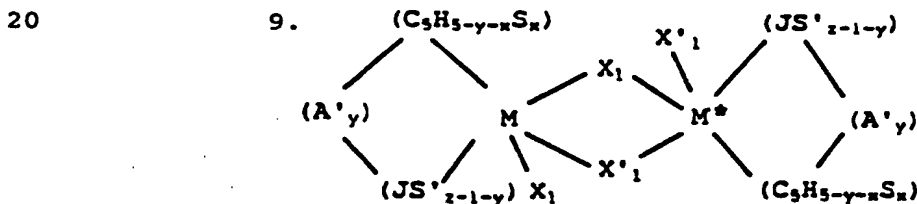
y is 0 or 1;

35  $(C_5H_{5-y-x}S_x)$  is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

( $JS_{z-1-y}$ ) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2, S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal centers M and M\* are bridged by  $X_1$  and  $X'_1$ , wherein M\* has the same meaning as M and  $X'_1$  has the same meaning as  $X_1$  where such dimeric compounds which are precursors to the cationic portion of the catalyst are represented by formula 4;



wherein:

w is an integer from 0 to 3; and

$X_1$  and  $X_2$  are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted Group 15 element radicals, or substituted Group 16 element radicals; or  $X_1$  and  $X_2$  are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or  $X_1$  and  $X_2$  together can be an olefin, diolefin or aryne ligand; or when

30

35

Lewis-acid activators are used,  $X_1$  and  $X_2$  can also be joined to form an anionic chelating ligand or can independently be any mono-valent anionic ligand including halides.

5           Table 1 depicts representative constituent  
moieties for the metallocene components of formulae 6-  
9. The list is for illustrative purposes only and  
should not be construed to be limiting in any way. A  
number of final components may be formed by permuting  
10 all possible combinations of the constituent moieties  
with each other. Illustrative compounds of the formula  
6 type are: bis(cyclopentadienyl)hafnium dimethyl,  
ethylenebis(tetrahydroindenyl)zirconium dihydride,  
bis(pentamethyl)zirconium ethylidene, dimethylsilyl(1-  
15 fluorenyl)(cyclopentadienyl)titanium dichloride and the  
like. Illustrative compounds of the formula 7 type  
are: bis(cyclopentadienyl) (1,3-butadiene(zirconium)),  
bis(cyclopentadienyl) (2,3-dimethyl-1,3-butadiene)  
zirconium, bis(pentamethylcyclopentadienyl) (benzene)  
20 zirconium, bis(pentamethylcyclopentadienyl) titanium  
ethylene and the like. Illustrative compounds of the  
formula 8 type are: (pentamethylcyclopentadienyl)  
(tetramethylcyclopentadienylmethylene) zirconium  
hydride, (pentamethylcyclopentadienyl)  
25 (tetramethylcyclopentadienyl)-  
(tetramethylcyclopentadienylmethylene) zirconium phenyl  
and the like. Illustrative compounds of the formula 9  
type are: dimethylsilyl(tetramethylcyclopentadienyl)  
(t-butylamido)zirconium dichloride,  
30 ethylene(methylcyclopentadienyl) (phenylamido)titanium  
dimethyl,  
methylphenylsilyl(indenyl) (phenylphosphido)hafnium  
dihydride and (pentamethylcyclopentadienyl) (di-t-  
butylamido)hafnium dimethoxide.

For illustrative purposes, the above compounds and those permuted from Table 1 include the neutral Lewis base ligand (L'). The conditions under which complexes containing neutral Lewis base ligands such as ether or those which form dimeric compounds is determined by the steric bulk of the ligands about the metal center. For example, the t-butyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$  has greater steric requirements than the phenyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NPh})\text{ZrCl}_2\text{Et}_2\text{O}$  thereby not permitting ether coordination in the former compound in its solid state. Similarly, due to the decreased steric bulk of the trimethylsilylcyclopentadienyl group in  $[\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-t-Bu})\text{ZrCl}_2]_2$  versus that of the tetramethylcyclopentadienyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$ , the former compound is dimeric and the latter is not.

TABLE 1

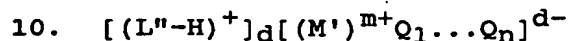
(A')	(C <sub>5</sub> H <sub>5</sub> -Y-X) <sub>n</sub>	(JS' <sub>2</sub> -1-Y)	X <sub>1</sub> or X <sub>2</sub> (B - Lewis Acid)	M
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride	zirconium
diethylsilyl	3,4-dimethylcyclopentadienyl	phenylamido	methyl	hafnium
di-n-propylsilyl	2,5-dimethylcyclopentadienyl	p-n-butylphenylamido	ethyl	titanium
di-isopropylsilyl	2-indenyl	cyclohexylamido	phenyl	
di-n-butylsilyl	3,4-diethylcyclopentadienyl	perfluorophenylamido	n-propyl	
di-t-butylsilyl	2,5-diethylcyclopentadienyl	n-butylamido	isopropyl	
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	n-butyl	
methylphenylsilyl	tetraethylcyclopentadienyl	ethylamido	amyl	L or L'
ethylmethylsilyl	tetra-n-propylcyclopentadienyl	n-propylamido	isoamyl	ethylene
diphenylsilyl	3,4-di-n-butylcyclopentadienyl	isopropylamido	hexyl	propylene
di(p-t-butylphenethylsilyl)	3,4-dicyclohexylcyclopentadienyl	benzylamido	isobutyl	1-butene
n-hexylmethylsilyl	2,5-di-n-butylcyclopentadienyl	cyclododecylamido	heptyl	1,4-hexadiene
cyclopentamethylsilyl	2,5-dicyclohexylcyclopentadienyl	s-butylamido	octyl	1,3-butadiene
cyclooctamethylsilyl	3-n-octyl-4-n-hexylcyclopentadienyl	t-butylphosphido	nonyl	1,3-hexadiene
cyclotrimethylsilyl	2-tetrahydroindenyl	ethylphosphido	decyl	acetylene
dimethylgermany	3-ethyl-4-n-propylcyclopentadienyl	phenylphosphido	cetyl	methylacetylene
diethylgermany	3-isopropyl-4-t-butylcyclopentadienyl	cyclohexylphosphido	chloro	benzene
phenylamido	3-phenyl-4-benzylcyclopentadienyl	oxo	fluoro	diethylether
methylamido	2,5-diphenylcyclopentadienyl	sulfido	bromo	dimethylether
t-butylphosphido	3,4-bis(trimethylgermyl)cyclopentadienyl	methoxide	iodo	trimethylamine
ethylphosphido	bis(trimethylstanny)cyclopentadienyl	ethoxide	methoxy	triethylamine
phenylphosphido	bis(trimethylplumbyl)cyclopentadienyl	methylthio	ethoxy	triethylamine
methylene	bis(trimethylstanny)cyclopentadienyl	dimethylthio	propoxy	triethylamine
diethylmethylene	bis(trimethylplumbyl)cyclopentadienyl	diphenylamide	butoxy	phosphine
ethylene	2-ethyl-5-n-propylcyclopentadienyl	methylphenylamide	phenoxy	tetrahydrofuran
dimethylethylene	2-methyl-5-t-butylcyclopentadienyl	dicyclohexylphosphido	dimethylamido	thiophene
dipropylethylene	2,5-bis(trimethylsilyl)cyclopentadienyl	diphenylphosphido	diethylamido	dimethylsulfide
propylene	3,4-bis(trimethylsilyl)cyclopentadienyl	bis(trimethylsilyl)-amido	methylamido	
dimethylpropylene	3,4-bis(N,N-dimethylamido)cyclopentadienyl	trimethylsilyloxy	diphenylphosphido	
1,1-dimethyl-3,3-dimethylpropylene	3,4-bis(dimethylphosphido)cyclopentadienyl		dicyclohexylphosphido	
tetramethyldisiloxane	cyclopentadienyl		dimethylphosphido	
1,1,4,4-tetramethyldisilyl ethylene	3,4-dimethylcyclopentadienyl		ethyleneglycol	
	3,4-dimethoxycyclopentadienyl		dianion (both X)	
	2,5-dimethyl-3,4-diethylcyclopentadienyl		methylidene (both X)	
	2,5-diethyl-3,4-dimethylcyclopentadienyl		ethylidene (both X)	
	2,5-dimethyl-3,4-diethylcyclopentadienyl		propylidene (both X)	

**B. The Activator Component**

Ionic catalysts can be prepared by reacting a transition metal compound with some neutral Lewis acids, such as  $B(C_6F_6)_3$  or an alumoxane, which upon  
5 reaction with the hydrolyzable ligand (X) of the transition metal compound forms an anion, such as  $([B(C_6F_5)_3(X)]^-)$ , which stabilizes the cationic transition metal species generated by the  
10 reaction. Ionic catalysts can be, and preferably are, prepared with activator components which are ionic compounds or compositions.

Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is  
15 preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4  
20 cation) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases  
such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been disclosed  
25 in copending U.S. Patent Application Nos. 133,052 and 133,480: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a  
30 plurality of boron atoms such as carboranes, metallacarboranes and boranes.

In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following  
35 general formula:



wherein:



H is a hydrogen atom;

[L"-H] is a Bronsted acid;

M' is a metal or metalloid;

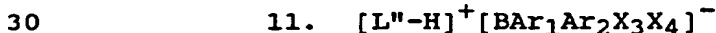
Q<sub>1</sub> to Q<sub>n</sub> are, independently, bridged or unbridged  
 5 hydride radicals, dialkylamido radicals, alkoxide and  
 aryloxy radicals, hydrocarbyl and substituted-  
 hydrocarbyl radicals, halocarbyl and substituted-  
 halocarbyl radicals and hydrocarbyl and halocarbyl-  
 substituted organometalloid radicals and any one, but  
 10 not more than one, of Q<sub>1</sub> to Q<sub>n</sub> may be a halide radical;

m is an integer representing the formal valence  
 charge of M; and

n is the total number of ligands q.

As indicated above, any metal or metalloid capable of  
 15 forming an anionic complex which is stable in water may  
 be used or contained in the anion of the second  
 compound. Suitable metals, then, include, but are not  
 limited to, aluminum, gold, platinum and the like.  
 Suitable metalloids include, but are not limited to,  
 20 boron, phosphorus, silicon and the like. Compounds  
 containing anions which comprise coordination complexes  
 containing a single metal or metalloid atom are, of  
 course, well known and many, particularly such  
 compounds containing a single boron atom in the anion  
 25 portion, are available commercially. In light of this,  
 salts containing anions comprising a coordination  
 complex containing a single boron atom are preferred.

The preferred activator compounds comprising boron  
 may be represented by the following general formula:



wherein:

B is a boron in a valence state of 3;

Ar<sub>1</sub> and Ar<sub>2</sub> are the same or different aromatic or  
 substituted-aromatic hydrocarbon radicals containing  
 35 from about 6 to about 20 carbon atoms and may be linked  
 to each other through a stable bridging group; and

X<sub>3</sub> and X<sub>4</sub> are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted Group 15 element radicals, substituted Group 16 element radicals and halide radicals, with the proviso that X<sub>3</sub> and X<sub>4</sub> will not be halide at the same time.

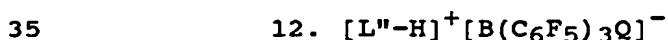
In general, Ar<sub>1</sub> and Ar<sub>2</sub> may, independently, be any aromatic or substituted-aromatic hydrocarbon radical. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy and aryloxy radicals, alkylamido radicals, fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as X<sub>3</sub> and X<sub>4</sub>. The substituent may be ortho, meta or para, relative to the carbon atoms bonded to the boron atom. When either or both X<sub>3</sub> and X<sub>4</sub> are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as are Ar<sub>1</sub> and Ar<sub>2</sub>, or the same may be a straight or branched alkyl, alkenyl or alkynyl radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical. X<sub>3</sub> and X<sub>4</sub> may also, independently be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals, hydrocarbyl radicals and organometalloid radicals and the like. As indicated above, Ar<sub>1</sub> and Ar<sub>2</sub> could be linked to either X<sub>3</sub> or X<sub>4</sub>. Finally, X<sub>3</sub> and X<sub>4</sub> may also be linked to each other through a suitable bridging group.

Illustrative, but non-limiting, examples of boron compounds which may be used as an activator component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such

as triethylammonium tetra(phenyl)boron,  
 tripropylammonium tetra(phenyl)boron, tri(n-  
 butyl)ammonium tetra(phenyl)boron, trimethylammonium  
 tetra(p-tolyl)boron, trimethylammonium tetra(o-  
 5 tolyl)boron, tributylammonium  
 tetra(pentafluorophenyl)boron, tripropylammonium  
 tetra(o,p-dimethylphenyl)boron, tributylammonium te-  
 tra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-  
 tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium  
 10 tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium  
 salts such as N,N-dimethylanilinium  
 tetra(pentafluorophenyl)boron, N,N-diethylanilinium  
 tetra(phenyl)boron, N,N-2,4,5-pentamethylanilinium  
 tetra(phenyl)boron and the like; dialkyl ammonium salts  
 15 such as di(i-propyl)ammonium  
 tetra(pentafluorophenyl)boron, dicyclohexylammonium  
 tetra(phenyl)boron and the like; and triaryl  
 phosphonium salts such as triphenylphosphonium  
 tetra(phenyl)boron, tri(methylphenyl)phosphonium  
 20 tetra(phenyl)boron, tri(dimethylphenyl)phosphonium  
 tetra(phenyl)boron and the like.

Similar lists of suitable compounds containing  
 other metals and metalloids which are useful as  
 activator components may be made, but such lists are  
 25 not deemed necessary to a complete disclosure. In this  
 regard, it should be noted that the foregoing list is  
 not intended to be exhaustive and that other useful  
 boron compounds as well as useful compounds containing  
 other metals or metalloids would be readily apparent to  
 30 those skilled in the art from the foregoing general  
 equations.

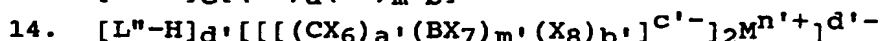
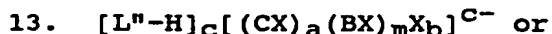
The most preferred activator compounds comprising  
 boron may be represented by the following general  
 formula:



wherein:

F is fluorine, C is carbon and B, L', and Q are defined hereinabove. Illustrative but not limiting, examples of most preferred activator compounds comprising boron which may be used in the preparation of the improved catalysts of this invention include N,N-dialkylanilinium salts (L' = N,N-dialkylaniline) where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymeric hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene, or poly-paramethylstyrene. Polymeric Q substituents on the most preferred anion offer the advantage of providing a highly soluble ion-exchange activator component and final ionic catalyst. Soluble catalysts and/or precursors are often preferred over insoluble waxes, oils, phases, or solids because they can be diluted to a desired concentration and can be transferred easily using simple equipment in commercial processes.

Activator components based on anions which contain a plurality of boron atoms may be represented by the following general formulae:



wherein

[L''-H] is either H<sup>+</sup> or a Bronsted acid derived from the protonation of a neutral Lewis base;

X, X', X'', X<sub>6</sub>, X<sub>7</sub> and X<sub>8</sub> are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, halocarbyl radicals, substituted-halocarbyl radicals, or hydrocarbyl- or halocarbyl-substituted organometalloid radicals;

M is a transition metal;

a and b are integers  $\geq 0$ ; c is an integer  $\geq 1$ ;  $a + a' + b + b' + c =$  an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22;

a and b are the same or a different integer 0; c is an integer  $\geq 2$ ;  $a + b + c =$  an even-numbered integer from 4 to about 8; m is an integer from 6 to about 12; n is an integer such that  $2ca - na = d$ ; and d is an integer  $\geq 1$ .

Preferred anions of this invention comprising a plurality of boron atoms comprise:

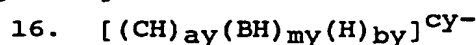
(1) A trisubstituted ammonium salt of a borane or carborane anion satisfying the general formula:



wherein:

ax is either 0 or 1; cx is either 1 or 2;  $ax + cx = 2$ ; and bx is an integer ranging from about 10 to 12;

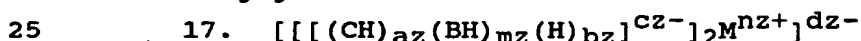
(2) A trisubstituted ammonium salt of a borane or carborane or a neutral borane or carborane compound satisfying the general formula:



wherein:

ay is an integer from 0 to 2; by is an integer from 0 to 3; cy is an integer from 0 to 3;  $ay + by + cy = 4$ ; and my is an integer from about 9 to about 18; or

(3) A trisubstituted ammonium salt of a metallaborane or metallacarborane anion satisfying the following general formula:



wherein:

az is an integer from 0 to 2; bz is an integer from 0 to 2; cz is either 2 or 3; mz is an integer from about 9 to 11;  $az + bz + cz = 4$ ; and nz and dz are, respectively, 2 and 2 or 3 and 1.

Illustrative, but not limiting, examples of second components which can be used in preparing catalyst systems utilized in the process of this invention wherein the anion of the second component contains a plurality of boron atoms (as in formulae 10-17) are mono-, di-, trialkylammonium and phosphonium and dialkylarylammonium and -phosphonium salts such as

bis[tri(n-butyl)ammonium] dodecaborate, bis[tri(n-butyl)ammonium]decachlorododecaborate, tri(n-butyl)ammonium dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium 1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadodecaborate, tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium dibromo-1-carbadodecaborate; borane and carborane complexes and salts of borane and carborane anions such as decaborane(14), 7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane, tri(n-butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate, tri(n-butyl)ammonium 7,8-dicarbaundecaborate and metallaborane anions such as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbaborate)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato) ferrate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato) cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaunaborato) nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato) ferrate(III), tri(n-butyl)ammonium bis(tribromooctahydrido-7,8-dicarbaundecaborato) cobaltate(III), tri(n-butyl)ammonium bis(undecahydridodicarbadodecaborato) cobaltate(III) and bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato) cobaltate(III). A similar list of representative phosphonium compounds can be recited as illustrative second compounds, but for the sake of brevity, it is simply noted that the phosphonium and substituted-phosphonium salts corresponding to the listed ammonium and substituted-ammonium salts could be used as second compounds in the present invention.

The preferred activator compounds comprising Lewis-acid activators and in particular alumoxanes are represented by the following general formulae:

18.  $(R^3-Al-O)_p$   
19.  $R^4(R^5-Al-O)_p-AlR^6_2$   
20.  $(M')^m+Q'_m$

An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are, independently a  $C_1-C_6$  alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "p" is an integer from 1 to about 50. Most preferably,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are, each methyl and "p" is a least 4. When an alkyl aluminum halide is employed in the preparation of the alumoxane, one or more  $R^{3-6}$  groups may be halide.  $M'$  and  $M$  are as described previously and  $Q'$  is a partially or fully fluorinated hydrocarbyl.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of a trialkyl aluminum with a limited amount of water yields a mixture of both linear and cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the catalyst systems of this invention are those prepared by the hydrolysis of a trialkylaluminum, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, dimethylaluminum chloride, diisobutylaluminum chloride, diethylaluminum chloride and the like. The most preferred alumoxane for use is methylalumoxane (MAO). Methylalumoxanes having an average degree of oligomerization of from 4 to 25 ("p")

= 4 to 25), with a range of 13 to 25 are the most preferred.

It is recognized that an alumoxane is not a discrete material. A typical alumoxane will contain free trisubstituted or trialkyl aluminum, bound trisubstituted or trialkyl aluminum, and alumoxane molecules of varying degree of oligomerization. Those methylalumoxanes most preferred contain lower levels of trimethylaluminum. Lower levels of trimethylaluminum can be achieved by reaction of the trimethylaluminum with a Lewis base or by vacuum distillation of the trimethyl aluminum or any other means known in the art.

It is also recognized that after reaction with the transition metal compound, some alumoxane molecules are in the anionic form as represented by equations 1-3, and thus for our purposes, are considered "non-coordinating" anions.

The activator compositions most preferred for forming the ionic catalyst used in this process are those containing a tetrapentafluorophenyl boron anion; two or more tripentafluorophenyl boron anion groups covalently bond to a central atomic molecular or polymeric complex or particle; tripentafluorophenyl boron; or methylalumoxane.

Other examples of activator specific compositions which may be used to form an anionic catalyst useful in this invention are identified and more fully described in European Patent Application Nos. 0 277 003 and 0 277 004 and WO 92/00333 which are hereby incorporated by reference.

#### CHOICE OF CATALYST

This invention relates to a process to produce long chain branched polymers, to catalysts used to produce long chain branched polymers and to the polymers themselves. This invention relates to a method for producing polymers with substantially linear



long chain branching comprising contacting, under polymerization conditions, a vinyl terminated polymer (macromonomer) with a chain length of 250 or more carbons, with one or more olefin monomers and a  
5 metalocene catalyst system comprising a mono, di, or tri cyclopentadienyl transition metal catalyst cocatalized with a non-coordinating anion or an alumoxane or a Lewis acid activator. This invention also contemplates a process for producing a branched  
10 polymer comprising:

contacting in the presence of a polymerization catalyst system,

(i) a macromonomer at least 250 carbons long comprising one or more C<sub>2</sub>-C<sub>30</sub> olefinic monomer units  
15 said macromonomer having chain end vinyl unsaturation, and

(ii) a polymerizable olefinic monomer or monomer mixture

under conditions to (co)polymerize the monomers  
20 and incorporate the macromonomer into the growing (co)polymer chain via the chain end unsaturation, said catalyst system comprising mono-, di-, or tri- cyclopentadienyl transition metal catalyst cocatalized with a non-coordinating anion, an aluminium  
25 alkyl, or an alumoxane.

The reaction is maintained at 70°C, more preferably 70 to 100°C, even more preferably at 90°C. The weight ratio of macromonomer to olefin monomer present is  
30 between about 1:1 to about 1:5, preferably about 1:1.5 to about 1:3, more preferably about 1:2.

The branched polymers of this invention are comprised of a family of polyolefins and olefin copolymers which are copolymerizable by metallocene polymerization. Long chain branched polymers of this  
35 type are made by copolymerization of vinyl terminated polymers with the desired ethylenically unsaturated monomer or monomers. The family of polyolefins

includes low to high density polyethylene or ethylene-  
alpha-olefin copolymers as well as polypropylene and  
polypropylene copolymers. The vinyl terminated  
polymers useful in this invention include high density  
5 polyethylene and polyethylene copolymers. Production  
of these polymers gives control over the side-chain  
molecular weight and composition. The branched  
polymers of this invention can be a low-density  
polyethylene with a high-density polyethylene branch.  
10 They are also not limited to side-chains consisting of  
the same polymer composition as the backbone. Likewise  
it is contemplated that the macromonomers can comprise  
homopolymers or copolymers of olefins, particularly of  
C<sub>2</sub> to C<sub>30</sub> alpha olefins. specifically a copolymer or  
15 polymer with more than 250 carbons that has vinyl  
termination can be used. The metallocene catalysts  
disclosed in this invention can produce vinyl-  
terminated homopolymers and copolymers. However,  
another method to produce vinyl termination is to  
20 produce a polymer with an ethylene "cap" or end with  
the needed vinyl group. This could be accomplished by  
raising the reaction temperature at the "end " of the  
reaction and simultaneously adding ethylene so that the  
ethylene preferentially polymerizes to form an end  
25 "cap" or block. A block copolymer of ethylene and a C<sub>3</sub>  
to C<sub>30</sub> alpha olefin would also present the necessary  
vinyl termination.

The main chain and the sidechains may be the same  
of different olefin homo or copolymers. In particular  
30 main and side chains of ethylene are preferred.  
However main and side chains of ethylene copolymerized  
with propylene, 1-butene, 1-pentene, 4-methylpentene-1,  
1-hexene or 1-octene are also preferred.

The ability to prepare long-chain branched olefins  
35 in which the side-chain compositions are significantly  
different from the backbone adds a unique dimension to  
the polymers of this invention

The branched polymers of this invention typically have a weight average molecular weight at or above 50,000, preferably 50,000 to 1,000,000 and a Mw/Mn of 6 or less. The vinyl terminated polymers (macromers) that become the side chains in the branched polymers of this invention are typically more than 200 carbons long, preferably 250 to 3500, even more preferably 300 to 3000 carbons long. Further these side chains insert into the main chain at an average of up to 5 side chains per 1000 main chain carbons, although it is statistically possible for a particular main chain to have no side chains. Also, as a benefit of utilizing titanium-containing monocyclopentadienyl transition metal catalysts in the catalyst system, a narrow composition distribution of the side chains may be obtained. A narrow composition distribution means that among the individual polymer main chains the number of side chains are roughly similar. For example, three main chains with 2, 3, and 2 side chains respectively have a very narrow composition distribution, while three main chains with 3, 9, and 20 sides chains, respectively, have a broad composition distribution. As an added benefit, if the main chain is a copolymer made using a titanium containing monocyclopentadienyl metallocene catalyst, it will have a narrow composition distribution and higher comonomer incorporation than traditional coordination catalysts.

It is also contemplated by this invention that the vinyl terminated macromonomer can be produced in one step of a continuous or series process which then proceeds to copolymerize the macromonomer with one or more alpha olefins. It is also contemplated that the macromonomer can be produced separately by one process and then polymerized later in a separate similar or different process.

CATALYSTS TO PRODUCE POLYMERS OF THE MACROMONOMER AND  
AN OLEFIN

A large group of metallocene catalysts may be selected from to produce both the vinyl terminated  
5 polymers (macromers) and the branched polymers of this invention. The choice of catalyst system is influenced by the characteristics desired in the final product. For example, a noncoordinating anion activation system rather than MAO could be found to be preferable to  
10 avoid isomerization problems, or the metallocene catalyst  $Cp_2ZrMe_2$  (bis cyclopentadienyl zirconium dimethyl) with  $(pfp)_3B$  (perflourotriphenyl boron) as the cocatalyst activator could be chosen because of this system's high activity at higher temperatures such  
15 as 90°C and above. Further this catalyst system gives high levels of vinyl ends during polymerization in hexane and few or no vinyl ends when polymerized in toluene. The resulting vinyl terminated polymers are branched. This branching can be eliminated if a  
20 sterically hindered catalyst like  $(Me_5Cp)_2ZrMe_2$  (bis pentamethylcyclopentadienyl zirconium dimethyl) is used. This catalyst system sterically inhibits the copolymerization of vinyl terminated polymers. It should be noted that the vinyl terminated macromonomers  
25 of this invention can be branched. However the level of this branching does not approach a dendritic structure. These macromers and those that have little or no side chain branching or are substantially linear will be referred to as linear.

30 The catalyst choices for copolymerization of vinyl terminated polymers with other monomers are also large and include catalyst systems containing bridged and unbridged bis cyclopentadienyl transition metal compounds as well as monocyclopentadienyl transition  
35 metal compounds. Monocyclopentadienyl transition metal catalysts are preferred as they polymerize large "monomers" well. For example, monocyclopentadienyl

(Mono Cp) transition metal catalysts, particularly titanium, incorporate more monomer than coordination catalysts. Thus one would choose a Mono Cp Ti catalyst to make lower density products over the

5 Tris(perfluorophenyl)Boron activated systems utilized in example 1 and 2 to make high density material.

To understand the advantages of polymers produced in accordance with the present invention, some general discussions of the properties of polymer solids and  
10 melts is helpful. Molten polyethylene is highly viscous. The viscosity is a function of weight-average molecular weight ( $M_w$ ); molecular weight distribution ( $M_w/M_n$ ), also called the index of polydispersity; and the shear rate exerted on the polymer. The molecular  
15 weight values are in part related to branching of the polymer. Molten polyethylene is classified as a pseudoplastic fluid, which means that its viscosity decreases with increasing shear rate. The relationship between viscosity and shear rate depends upon the  
20 molecular weight distribution and degree of long chain branching of the polymer. Polymers having a broad molecular weight distribution tend to have lower viscosity values at conditions of high shear rates than polymers having a narrow molecular weight distribution  
25 while having equivalent viscosities at conditions of low shear rates.

As noted, viscosity as a function of shear rate is also dependent upon the degree of long chain branching of a polymer which affects molecular weight  
30 distribution. In general, a polymer with long chain branching will have higher viscosity values at low shear rates and lower viscosity values at high shear rates compared to an unbranched polymer with equivalent molecular weight. Lower viscosity at high shear rates  
35 means the long chain branched polymer can be extruded at lower temperatures and at a higher rate which results in less energy consumption.

From a processability viewpoint, it is usually desirable to have a polymer which displays high viscosity at low shear rates and low viscosity at high shear rates, in other words, it is desirable to have a polymer that processes with the characteristics of a branched polymer at conditions of low shear while having the processing characteristics of a broad molecular weight distribution branched polymer at conditions of high shear. This combination of properties is often sought by broadening the molecular weight distribution of a polymer by introducing long chain branching.

The inventors have found that the positive viscosity processing characteristics of a polymer at both ends of the shear rate range may be achieved by polymers in accordance with the present invention. The predictable solid polymer mechanical properties achievable by polymers in accordance with the present invention are good impact and tear resistance, good environmental stress crack resistance (ESCR) values, good tensile properties, good modulus/density balance, good reblock/density balance, and good clarity, relative to linear polyethylenes without long chain branching.

This unique balance of favorable polymer melt processability and solid polymer mechanical characteristics is achieved through the creation of remote long chain branching at a frequency and length great enough to impart processability characteristics of LDPEs but at a low enough frequency so as not to destroy the superior solid polymer physical characteristics of LPEs. In particular, this balance is achieved by the introduction of some linear long chain branches having a average molecular weight greater than the critical molecular weight for entanglement ( $M_c$ ) of the polymer with a linear long chain branching frequency less than 5.0 branches per

1,000 carbon atoms of the main polymer chains. These polymers may be produced over a wide range of molecular weight distributions ( $M_w/M_n$ ) (index of polydispersity) of 2.0 to 10. Preferably, the frequency of long chain  
5 branching is less than 5 branches per 1,000 carbon atoms of the main polymer chains (preferably an average frequency of 0.2 to 3 chains per 1000 C, atom, even more preferably an average frequency of 0.9 to 2 chains per 1000 C, even more preferably an average frequency  
10 of 1 to 2 chains per 1000 C) with a preferred molecular weight distribution range of about 2 to about 6, more preferably 2 to 4.

These advantageous properties can be achieved when even 5 or more weight percent of the composition is  
15 "branched." This may occur when a branched polymer is blended with another polymer or when the branched polymer is part of a reactor blend. Preferably the branched polymer is present at least 5 weight percent, even more preferably at least 10 weight percent, even  
20 more preferably at least 40 to 70 weight percent.

The viscosity characteristics of polymers of the present invention are not the only processing advantages. Another advantage of polymers having linear long chain branching in accordance with the  
25 present invention are the superior elastic characteristics of the polymer melt. Molten polyethylene exhibits elastic properties over a wide temperature range. After molten polyethylene passes through the die of an extruder under pressure, the  
30 strand of polyethylene increases in diameter or thickness. This is known as extrudate swell. At low shear rates, extrudate swell increases as molecular weight and long chain branching increase. In other words, extrudates typically swell as molecular weight  
35 distribution broadens.

Polymers produced in accordance with the present invention exhibit increased extrudate swell. The

significance of this increased extrudate swell is that is a reflection of what is known as the elastic nature of the polymer. The elastic nature of the polymer is very important in certain polymer melt extrusion processes such as the manufacture of tubular film, chill roll casting and extrusion coating in which an extruded web of film is produced which is stretched in the direction of flow. Such extrusion processes can only be carried out with materials that are able to sustain a tensile stress on the melt. In other words, it is important that the polymer melt be somewhat elastic. There should be a balance between the elasticity of the polymer melt and the viscosity in blow molding operation. The balance between elasticity and viscosity of the polymer melt affects polymer parison integrity. If the balance of properties is in favor of viscosity over elasticity, the polymer melt will not have good stability and tend to sag during certain extrusion processes. There is a strong correlation between extrudate swell ratios and parison integrity. The introduction of long chain branching in accordance with the present invention results in polymer melts having swell ratios indicative of good elastic properties for extrusion processes.

The presence of a small amount of long chain branching in a linear molecule increases elasticity of the polymer melt by introducing very long relaxation times in the relaxation spectrum of the melt. Since the polymer melt is a collection of molecules with different lengths and different branches, each molecule will respond differently to a given deformation. The collection of response times is referred to as the relaxation time spectrum which directly relates to the stability of the polymer melt during extrusion.

Long chain branching in accordance with the present invention has another important advantage of changing the elongational characteristics of polymer



melts. The presence of long chain branching increases the value of the longational viscosity and introduces a maximum elongation viscosity as a function of strain rate.

5           The polymers produced in accordance with the present invention have still another advantage of having a reduced tendency to melt fracture at high shear rates. Smooth extrudates of polymer melts may be obtained easily at low shear rates. However, above a  
10       critical shear rate, the extrudate becomes uneven. The form of distortion of the extrudate varies. In some cases, the extrudate has the form of a screw thread, in others, the extrudate becomes spiral twisted while in others the distortion may take on the affect of a  
15       regular ripple or even random distortions. The critical shear rate of a polymer is related to the degree of entanglement of the polymer. The greater the degree of entanglement of the polymer, the lower the critical shear rate. Since the polymers produced in  
20       accordance with the present invention, due to the linear long chain branching, have less entanglement than linear polymers, the critical shear rate of these polymers will be increased. The result is that  
25       polymers made in accordance with the present invention have a reduced tendency to melt fracture at high shear rates than conventional linear polymers.

          The polymers of the present invention also enjoy the good solid polymer mechanical properties associated with short chain branching distributions of single  
30       site catalyst polymerizations. The polymers produced in accordance with the present invention may have high molecular weights with narrow molecular weight  
      distributions. These narrow distributions result in products having lower extractables caused by amorphous  
35       waxes, better clarity due to the absence of large light refracting crystals, and superior impact resistant due

to increased number of tie molecules binding crystal regions together.

The frequency of chain branching is determined by <sup>13</sup>C NMR spectrometry for homopolymers and by measuring the viscous energy of activation of copolymers with a parallel plate oscillating shear melt rheometer.

Long chain branching may be detected by comparing the results of different gel permeation chromatography (GPC), measured with both a refractive index detector and a low angle laser light scattering detector. GPC separations are governed by the hydrodynamic volume of polymeric molecules in solution. The standard detector on most GPCs measures the relative refractive index (RI) of the effluent. The RI detector assumes that molecules coming off the separation column at Time 1 have the same molecular weight as molecules eluting from an unbranched calibration standard at Time 1. It has been discovered that long chain branches do not increase the hydrodynamic volume of a molecule by an amount proportional to the length of its branches. It is believed that the contribution in the hydrodynamic volume is only a fraction of the branch length. In other words, refractive index detectors cannot "see" linear long chain branches in accordance with the present invention. However, a low angle light scattering (LALLS) detector does "see" all carbons in a polymer molecule. By analyzing a sample with both detectors, the difference in the results provides evidence of long chain branching in accordance with the present invention. This technique is illustrated by the following data:

Sample	Mw (DRI detector)	Mw (LALLS detector)
A	99800	99900
B	111000	116000
C	206000	231000

Sample A is an ethylene-hexene copolymer made in a gas phase process with a metallocene catalyst which is known to have no long chain branches. By comparing the molecular weight values calculated by the standard refractive index detector (RI) and the LALLS detection method, one sees that there is no significant difference in the values suggesting there are no hidden branches. Comparing the RI and LALLS values for sample B, an increase of 5,000 in molecular weight is seen by the LALLS detection method. With sample C, a 25,000 molecular weight increase is detected. The higher molecular weight of samples B and C as determined with the LALLS detector are evidence of long chain branching.

By comparing the different GPC techniques for polymers in accordance with the present invention, one generally sees that molecular weight as calculated by the LALLS technique is greater than the molecular weight as calculated by the RI GPC technique.

Long-chain branching in polyethylene is defined as those branches which produce one or more of the following effects.

#### 1. High viscous energy of activation ( $E_a$ ).

Polymer viscous energy of activation can be determined with parallel plate shear melt rheometry. Melt viscosity-temperature dependence is determined by performing shear rate superposition. The resulting shift factors are fitted to an Arrhenius equation; the product is the viscous energy of activation.

The energies of activation for a variety of polyethylene types are illustrated in the bar chart of figure 1. HDPE represents narrow MWD, linear homopolymers in the 5-50 MI range. LLDPE represents narrow MWD, linear ethylene-butene copolymers with comonomer content ~12% and MI in the 1-2 dg/min range. HMW-HDPE represents narrow MWD, linear ethylene

homopolymers with Mw's greater than 200k (i.e., MI < 0.2 dg/min). LDPE represents long-chain branched, ethylene homopolymers produced in a free-radical process. The LPE w/ LCB represents some of the branched  
5 polymers of this invention.

The unusually high Ea of the LPE w/ LCB is clear evidence of long-chain branching.

10 **2. Low viscosity, moderate shear rates relative to unbranched NMWD linear polymers.**

Melt viscosities can be measured vs. shear rate with a capillary rheometer. Figure 2 is an illustration of the relationship between the Mw of NMWD linear polyethylenes, and their melt viscosity measured at  
15  $340 \text{ s}^{-1}$  and  $190^\circ\text{C}$ . This data is narrowly distributed about a linear model:  $\text{viscosity} = 0.0115 \times \text{Mw} - 325$ . The position of the LDPE samples reflects the known fact that LDPEs are more "shear thinning" than linear polyethylenes, i.e., their viscosities decrease more  
20 rapidly as shear rate increases than do the viscosities of linear polyethylenes. The position of the LPE w/ LCB is clear evidence that this NMWD linear homopolymer contains long-chain branching. The branched polymers of this invention have a viscosity measured at  $340 \text{ sec}^{-1}/190^\circ\text{C}$  of  $0.75(0.0115 \times \text{Mw} - 325)$ .  
25

**3. High melt strength.**

Melt strength can be determined with a Rheotens Instrument which consists of a capillary rheometer  
30 equipped with an accelerating wheel take-off station. The melt tensile force in the capillary rheometer extrudate is measured as a function of the instantaneous wheel velocity. Figure 3 illustrates the relationship between melt tension, measured at  $190^\circ\text{C}$   
35 immediately before the onset of severe draw resonance, and Mw for numerous unbranched, narrow MWD linear ethylene-alpha-olefin copolymers. These tensile forces

are narrowly distributed about a linear model: melt tensile force =  $(7.68 \times 10^{-5}) \times M_w - 4.32$ . The branched polymers of this invention will exhibit a melt tensile force of  $1.3((7.68 \times 10^{-5}) \times (M_w \text{ of the polymer}) - 4.32)$ .

The unusually high tensile force observed with the LDPE is attributed to its long-chain branching. Evidence of the maximum frequency of the long-chain branches in a linear polymer can be determined with carbon-13 NMR if the polymer contains no short-chain branches, due to the comonomer, which are larger than 3 carbons in length. The carbon atom in the polymer's backbone to which a branch, which is larger than 3 carbons in length, is attached produces a signal in the C13-NMR spectrum at 38 ppm, which is distinguishable from all other carbons in the qualifying test sample and therefore a measure of the maximum number of long-chain branch points.

The present invention may be illustrated by the following examples:

#### EXAMPLE 1 Macromer A

A one liter autoclave solution polymerization reactor was charged with 400 ml toluene, 40 psig ethylene, and 58.9mg  $Cp_2ZrMe_2$  & 11mg  $B(pfp)_3$  [Bis(cyclopentadienyl)Zirconiumdimethyl & tris(pentafluorophenyl) Boron]. The mixture was reacted at 90°C (16° exotherm) for 0.87 hours. The polymerization yielded 121.4 grams of polymer after drying in a vacuum oven for 24 hours until odor-free. The dried polymer consisted of irregularly-shaped particles ranging in size from less than 0.1 mm to greater than 1 cm. The density of the polymer was 0.953 g/cm<sup>3</sup>, with a weight-average molecular weight ( $M_w$ ) of 29,000 with a level of vinyl that was not detected by NMR, and an index of polydispersity ( $M_w/M_n$ ) of 3.28. The polymer had a chain branching frequency of 0.48 branches per 1,000

carbon atoms of the main polymer chains by  $^{13}\text{C}$  NMR analysis.

**EXAMPLE 2 Polymerization with Macromer A**

5           A one liter solution polymerization autoclave reactor was charged with 400ml toluene, 25g of macromer A produced in example 1 (linear ethylene homopolymer having a weight-average molecular weight ( $M_w$ ) of 29,000 with very low levels, i.e. not detected, of vinyl  
10           unsaturations per 1,000 carbon atoms) and 100 psig ethylene, and 0.24 millimoles of bis (cyclopentadiene) dimethyl zirconium tris (pentafluorophenyl) boron catalyst (in toluene) with an initial reactor temperature of 45°C. The solution temperature was  
15           raised to 102°C and reacted for 0.33 hours. The polymerization yielded 57.0 g of polymer after drying in a vacuum oven for 24 hours until odor-free. The dried polymer consisted of irregularly-shaped particles ranging in size from less than 0.1 mm to greater than  
20           1.0 cm. The density of the polymer was 0.953 g/cm<sup>3</sup>, with a weight-average molecular weight ( $M_w$ ) of 82,500 and an index of polydispersity ( $M_w/M_n$ ) of 5.3 The polymer had a long chain branching frequency of 2 long chain branches per 1,000 main chain carbon atoms by  $^{13}\text{C}$   
25           NMR analysis.

**EXAMPLE 3 Macromer B**

          A one liter autoclave solution polymerization reactor was charged with 400 ml of hexane, 20 psig  
30           ethylene, and 60 mg of bis (cyclopentadiene) dimethyl zirconium catalyst and 60 mg of tris (pentafluoronyl) boron catalyst activator. The mixture was reacted at 90°C for 0.7 hours. The polymerization yielded 26g of polymer after drying in a vacuum oven for 24 hours  
35           until odor-free. The weight-average molecular weight ( $M_w$ ) of the polymer was 21,000 and the index of polydispersity ( $M_w/M_n$ ) was 8.2. The polymer had a

chain branching frequency of 1.22 branches per 1,000 main chain carbon atoms of the main polymer chains by  $^{13}\text{C}$  NMR analysis.

5 **EXAMPLE 4 Polymerization with Macromer B**

A one liter autoclave solution polymerization reactor was charged with 400ml of toluene, 25g macromer B produced in example 3 (linear ethylene homopolymer having a weight-average molecular weight ( $M_w$ ) of 21,000 and 1.0 vinyl saturations per 1,000 carbon atoms) and 10 50 psig ethylene, and 0.24 milimoles bis (cyclopentadiene) dimethyl zirconium tris (pentafluorophenyl) boron catalyst (in toluene). The mixture was reacted at 60°C (42° exotherm) for 0.28 15 hours. The polymerization yielded 78.8g of polymer after drying in a vacuum oven for 24 hours until odor-free. The weight-average molecular weight ( $M_w$ ) was 32,000 and index of polydispersity or MWD, ( $M_w/M_n$ ) was 3.0. The polymer had a linear long chain branching 20 frequency of 0.48 branches per 1,000 carbon atoms of the main polymer chains by  $^{13}\text{C}$  NMR analysis.

**CLAIMS**

What is claimed is:

1. A branched polyolefin comprising:  
a main chain (b) of a homopolymer or a  
5 copolymer of C<sub>2</sub> - C<sub>30</sub> alpha olefins; and  
side chains (a) of at least 250 carbon atoms  
comprising a homopolymer or a copolymer of C<sub>2</sub> -  
C<sub>30</sub> alpha olefins, said side chains being  
distributed along the polymer main chain at an  
10 average frequency of 0.1 to 5 side chains per 1000  
main chain carbon atoms,  
said branched polymer having a weight average  
molecular weight of at least 30,000 and an  $M_w/M_n$   
of 6 or less.  
15
2. The branched polyolefin of claim 1 wherein the side  
chains(a) are 300 to 3000 carbons long.
3. The branched polyolefin of claim 1 or 2 having a  $M_w$   
20 of 30,000 to 1,000,000.
4. The branched polyolefin of any previous claim  
having a  $M_w/M_n$  between 1 and 4.
- 25 5. The branched polyolefin of any previous claim  
having side chains(a) present at an average frequency  
of 0.2 to 3 side chains per 1000 main chain carbons.
6. The polyolefin of any previous claim wherein the  
30 side chains (a) derive from ethylene and any C<sub>3</sub> to C<sub>30</sub>  
alpha olefin and the main chain, independently, derives  
from ethylene and any C<sub>3</sub> to C<sub>30</sub> alpha olefin.
7. The branched polymer of any previous claim  
35 characterized by a density of 0.85 to 0.95g/cm<sup>3</sup>.



8. The branched polymer of any previous claim wherein the side chains (a) comprise block copolymer of ethylene and propylene.
- 5 9. The polymer of any previous claim wherein the side chains (a) comprise a polymer of any C<sub>3</sub> to C<sub>30</sub> alpha olefin with an ethylene block present at the insertion point along the main chain.
- 10 10. A polymer blend composition comprising at least 5 weight percent, based upon the weight of the composition, of a branched polyolefin of any previous claim.
- 15 11. A film or article of manufacture comprising the branched polymer of any previous claim.
12. A method for producing polyolefins of claims 1-10 comprising the steps of:
- 20 1) contacting under polymerization conditions :  
one or more alpha olefin monomers with a catalyst system to produce a vinyl terminated macromonomer of at least 250 carbon atoms long;
- 25 2) subsequently contacting, under polymerization conditions:  
said vinyl terminated macromonomer; with one or more alpha olefin monomers; and a catalyst system comprising a cyclopentadienyl transition metal catalyst and a cocatalyst or
- 30 activator.
13. The method of claim 12, wherein the transition metal is Zr, Hf, or Ti.

14. The method of claims 12 or 13, wherein the cocatalyst activator is an alumoxane or a Lewis acid activator.
- 5 15. The method of claims 12, 13, or 14 wherein the polymerization conditions for step 2) are solution, gas phase, bulk phase, or supercritical phase polymerization conditions.
- 10 16. A branched polyolefin of claim 1 having energy of activation greater than about 9 kcal/mole or a viscosity of  $0.75X(0.0115 \times Mw \text{ of the polymer } -325)$  and a melt strength  $1.3x((7.68 \times 10^{-5}) \times Mw-4.32)$ .
- 15 17. The method of claims 12 - 15, wherein the cyclopentadienyl transition metal catalyst is a transition metal compound comprising a single cyclopentadienyl group and a heteroatom containing group each bonded to the transition metal, said  
20 cyclopentadienyl group and heteroatom containing groups optionally bridged through a divalent moiety.

**INTERNATIONAL SEARCH REPORT**

Inter. Appl. Application No  
**PCT/US 93/08833**

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 5 C08F299/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,91 17194 (EXXON CHEMICAL PATENTS) 14 November 1991 see page 9, line 20 - line 26 see page 12, line 1 - line 28 ---	1
A	EP,A,0 366 411 (EXXON CHEMICAL PATENTS) 2 May 1990 ---	1
A	WO,A,92 00333 (EXXON CHEMICAL PATENTS) 9 January 1992 cited in the application ---	1, 12
A	EP,A,0 129 313 (EXXON RESEARCH AND ENGINEERING) 27 December 1984 cited in the application & US,A,4 500 648 ---	1
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Further documents are listed in the continuation of box C.       Patent family members are listed in annex.

\* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search <b>29 December 1993</b>	Date of mailing of the international search report <b>13. 01. 94</b>
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer <b>Andriollo, G</b>
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INTERNATIONAL SEARCH REPORT

Inter. Application No  
PCT/US 93/08833

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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information on patent family members

International Application No

PCT/US 93/08833

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